16p.

STUDY OF IMPROVED BERYLLIUM OXIDE MATERIALS FOR MICROELECTRONICS TECHNOLOGY

N64-20815

CAT. 19 - Code 1

NASA CR 56190

Bi-Monthly Report for the
Period 1 July - 31 August 1963
Contract NASw-685

Submitted by
National Beryllia Corporation
Haskell, New Jersey

OTS PRICE

XEROX $ 1.60 ph

to
National Aeronautics and Space Administration
Washington 25, D. C.

September 15, 1963

NASw-685

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(1) INTRODUCTION

The use of beryllium oxide in single crystal form as a substrate for microelectronic devices and integrated circuitry is predicated on the fact that this material, while being an excellent dielectric, displays extremely high thermal conduction values. As such it can provide heat dissipation, allowing the application of higher power levels and resulting in increased reliability in devices in which it is used. As described in the previous bi-monthly report, data measured on polycrystalline beryllium oxide ceramic materials has been supported by subsequent device and package use leading to increased performance of semi-conductor materials.

Knowledge of the basic crystal structure of beryllium oxide leads to the conclusion that because of its anisotropic character the material in crystal form should display directional thermal conducting properties combined with dielectric properties far superior to those found in the polycrystalline material. This is analagous to the improved behavior of sapphire over conventional polycrystalline aluminum oxide.

The present program has as an objective the development of techniques for the growth of beryllium oxide in single crystal form suitable for use in microelectronic devices and the accurate determination of thermal and electrical properties of these crystals with additional supporting data as required. The program is being conducted under the following Tasks:

Task A - Single Crystal Growth

Conduct an experimental investigation with the objective of perfecting the reproducibility of beryllium oxide single crystals with optimum surface smoothness and electrical homogeniety by controlling the crystal growth, chemistry and geometry.

Task B - Dielectric, Optical and Thermal Properties

Determine the precise dielectric, optical, and thermal properties of beryllium oxide single crystals. This shall include measurement of anisotropic behavior of dielectric constant, resistivity, and thermal conductivity, the data being applicable to a wide range of applications. Measurements shall also be made of optical and microwave properties as they are applied to microcircuitry.

(2) TECHNICAL PROGRAM

Task A - Single Crystal Growth

Study of the growth of the single crystals of beryllium oxide is being pursued along two primary lines of endeavor. These are: growth of BeO crystals by the water-vapor transport technique, which utilizes the generation of $Be(OH)_2$ vapor from a BeO nutrient with a subsequent condensation on a seed surface at elevated temperatures; the second technique is an exploratory study of the flux growth method utilizing alkali molybdate solvents. Both of these techniques have a fair degree of promise for preparation of dielectric BeO crystals and are being explored under this task of the contract.

(1) Water-Vapor Transport Growth Method

During the reporting period, experimental runs were continued on the growth of beryllium oxide single crystals using the high temperature induction apparatus previously described. Figure (1) is a list of typical processing data for these growth studies.

The objective of these series of experiments has been to vary the conditions of temperature, time, and carrier gas dew point and to study their effect on the yield and quality of resultant crystals. It has been found that optimum growth conditions occur when the following conditions are met:

a. The reaction zone is constructed of completely pure polycrystalline beryllium oxide to minimize impurities present in the system.

b. Nutrient material utilized as a source for beryllium hydroxide is high purity sintered beryllium oxide grit or scraps and the seed material is also beryllium oxide.

c. Induction heating through the use of the graphite susceptor system is initiated with very rapid heating rated on the order of 7°C/minute.

d. Water vapor is introduced at a temperature of 1200°C into the reaction zone using helium as a carrier gas.

e. Water flow rates are on the order of 2 cc per minute.

f. Vaporizer bath temperatures are on the order of 180°C.

g. The high temperature reaction zone where evaporation of the beryllia occurs lies between 1775 and 1825°C.

h. A reaction holding time of 2½ hours is utilized.

Using this process it has been found possible to reproducibly prepare beryllia single crystals in hexagonal platelet form up to sizes of approximately 3/16" which appear to be suitable for initial dielectric measurements. The objective of the continuing experiments is to

FIGURE 1

EXPERIMENTAL CRYSTAL GROWTH RUNS

Run No.	Carrier Gas	Gas Flow Rate	Vaporizer Temp.	H_2O Flow Rate	Operating Temperature	Time at Temperature	Results
12	He	1 L/min	175°C		1900°C	2 hr 30 min	No crystals
13	He	1 L/min	170°C		1900	2 hr 30 min	Some crystal growth
14	He	1 L/min	175°C	1 cc/min	1900	2 hr 30 min	Fibers on exit end of reaction tube
15	He	1 L/min	170°C	1 cc/min	1850	2 hr 30 min	Some growth at ends of reaction tube
16	He	1 L/min	185°C	1 cc/min	1850	2 hr 30 min	Fibrous growth on rod numerous small plate-lets
17	He	1 L/min	185°C	2 cc/min	1800	2 hr 30 min	Good yield of plate-lets on seed rod

yield increased crystal size, and to accomplish this several factors must be overcome. These factors include the close control of seed surface conditions so as to yield platelets in the proper section of the reaction chamber, the reaction chamber temperature, and the vaporizer temperature as it controls the water content of the carrier gas. Variations of as little as $\pm 5^{o}C$ in the vaporizer temperature have been found to modify crystal habit from either a fibrous or cotton-like condensate to the platelet structure which is desired.

(2) Solution Growth Experiments

The furnace system being utilized for solution growth consists of a platinum-wound (aluminum oxide) muffle, controllable to temperatures up to 1550°C. Initial tests utilizing lithium dimolybdate flux materials have been conducted at furnace operating temperatures of 1400°C. The container used consists of a sintered beryllium oxide boat with a high purity platinum liner to minimize reactivity with the container material. At this time the initial experiments have been conducted utilizing solution times on the order of several days. Modification of the furnace control system has been undertaken to reduce flucuations within the hot zone and experiments are continuing on the introduction of an artificial gradient for controlling the growth direction. While crystals have not yet been obtained by this technique it is felt that the initial experimental yield will be avaible in the very near future.

Task B - Dielectric, Thermal and Optical Properties

(1) Dielectric Properties

In the previous report a description was given of the measurements which are to be made of single crystal BeO platelets. These include volume resistivity, capacitance and dissipation factor. The basic equipment being utilized includes a Federal Model H Teraohmmeter for DC resistivity, a General Radio 1615A capacitance bridge assembly and a Boonton Radio 160A Q-meter. Because of the limited size of crystal samples available, a major portion of the effort has been devoted to the design and construction of a sample holder capable of measuring the capacitances of extremely fine gaps with reproducibility and precision. To achieve this, a preliminary sample holder (model no.1) was constructed and exploratory measurements made with the General Radio bridge in order to determine what some of the problem areas would be in working with such a system. Based on these preliminary experiments which were briefly described in the previous bi-monthly report it was determined that such a measurement apparatus would have the following requirements.

(a) Capability of adjustment and calibration of capacitance gap openings down to .0001" (2.5 microns).

(b) Complete flexibility in adjustment of probe and ground electrode location so as to allow measurement of not only platelet type materials but ultimately fibrous crystals.

(c) Facility for adapting the sample holder to high temperature measurements without disturbing the major electrical characteristics of the system.

(d) A design made such that the extremely small platelet crystals can be inserted and removed with a minimum of handling and with their location being such that they can be physically observed before, during, and after the measurements have been taken.

With these parameters in mind the present apparatus was designed and the device is shown in Figure (2). During the reporting period the apparatus was completed and was put into operation. Initial measurements have been made on simulated crystals fabricated from polycrystalline BeO discs. These samples consist of pressed and sintered BeO of 99% purity and 95% density and have been prepared in the following dimensions:

Type	Diameter (in)	Thickness (in)	Electrodes
P-1	.177	.020	None
P-2	.123	.012	None
P-3	.096	.035	Mo-Mn/Gold Plate
P-4	.052	.021	None
P-5	.400	.042	Mo-Mn/Ni Plate
P-6	.500	.020	Mo-Mn/Cu Plate
P-7	.140	.025	Mo-Mn/Cu Plate

Comparative tests were conducted on metallized and un-metallized BeO disc samples and it was determined that it would be a necessity in subsequent testing to apply metallic electrodes to the sample under test. This was found to be necessary so as to define closely the electrode area under measurement. Considerable scatter was found in those samples tested without electrodes in which the probe electrode alone was relied upon for contact. Techniques are available for the application of these electrodes to the BeO single crystal body either by vacuum deposition or sputtering and will be applied at such time that the tests on the crystals are conducted. Figure (3) shows some of the initial dielectric data obtained on the BeO electrode substrate materials, using Model No. 1 and No. 2 experimental apparatu

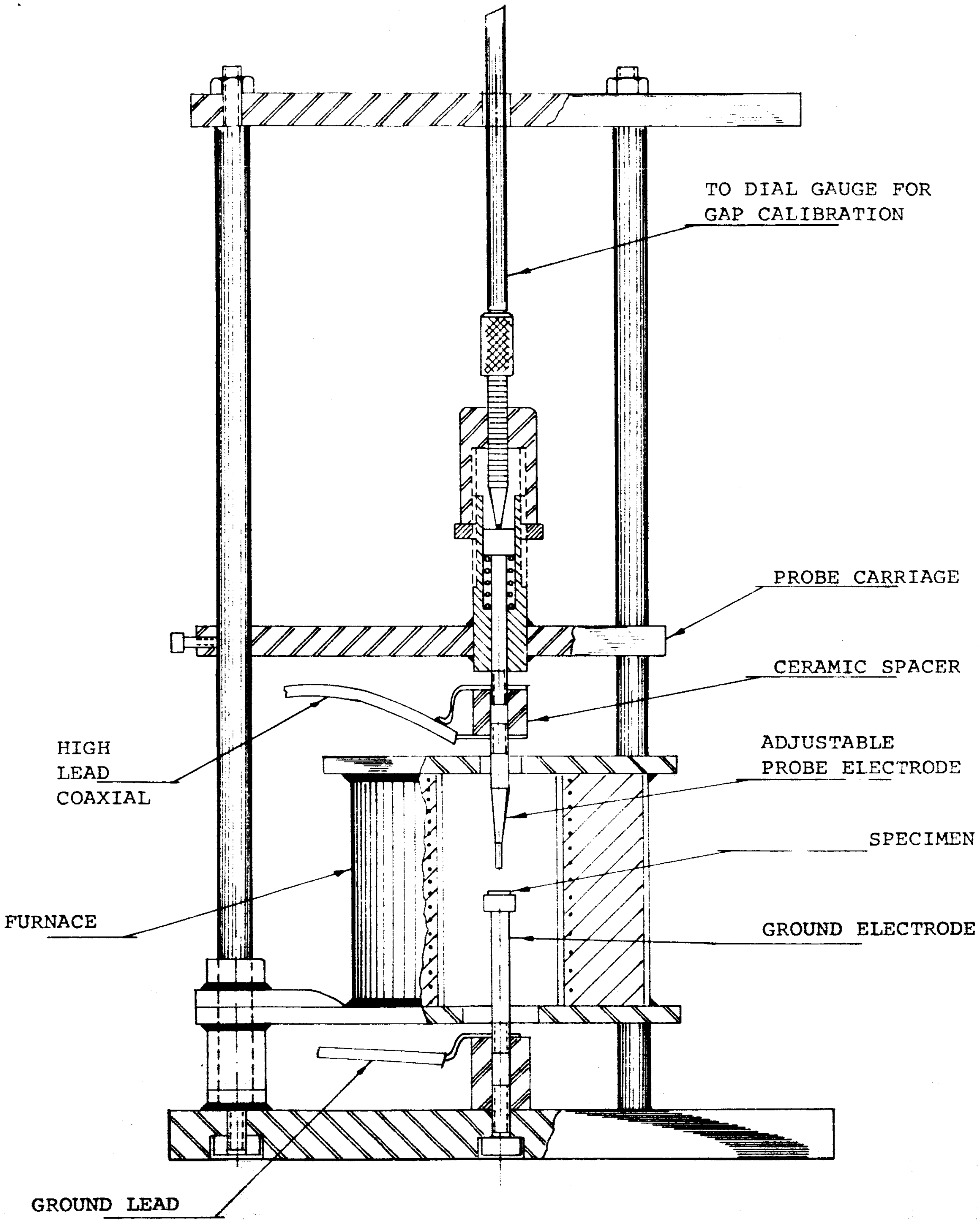


FIGURE 2

BeO CRYSTAL DIELECTRIC SAMPLE HOLDER NO. 2

FIGURE 3

PRELIMINARY DIELECTRIC MEASUREMENTS OF BERYLLIA SAMPLES AT 25°C

Sample Holder No. 1

Description of Sample	Frequency f	C_2 (Picofarads)	C_1 (Picofarads)	C_x (Picofarads)	D_2	D_1	Dielectric Constant K
(a) BeO Disc Type P-5 Metallized w/Ni Plate	1 KC	.7600	5.5200	4.7600	.0090	.0030	7.19
(b) BeO Disc Type P-5 Metallized w/Ni Plate	1 KC	.7500	5.3290	4.5790	.0090	.0030	6.90
(c) BeO Disc Type P-6 Metallized w/Cu Plate	1 KC	.7752	19.4000	18.6248	.0100	.0050	8.49
(d) BeO Disc Type P-6 Metallized w/Cu Plate	1 KC	.7730	17.7300	16.9520	.0096	.0100	7.85
(e) BeO Disc Type P-6 Metallized w/Cu Plate	1 KC	.7866	17.5900	16.8034	.0200	.0010	7.83
(f) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	.7686	1.1680	0.3994	.0100	.0100	8.09

Sample Holder No. 1
cont.

Description of Sample	Frequency f	C_2	Picofarads C_1	C_x	D_2	D_1	Dielectric Constant K
(g) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	.7580	1.1940	0.4360	.0100	.0100	8.90
(h) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	.7749	1.1853	0.4104	.0100	.0120	8.42
(i) Beo Disc Type P-7 Metallized Mo-Mn only	1 KC	.7904	1.6176	0.8272	.0100	.0050	6.36
(j) BeO Disc Type P-7 Metallized Mo-Mn only	1 KC	.7740	1.5947	0.8207	.0100	.0050	6.31
(k) BeO Disc Type P-7 Metallized Mo-Mn only	1 KC	.7777	1.5818	0.8041	0.100	.0050	6.41

Sample Holder No. 2 (Without Sample Shield)

Description of Sample	Frequency f	Picofarads C_2	C_1	C_x	Dielectric Constant K
(a) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	17.3700	17.7500	.3800	7.69
(b) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	17.3600	17.7600	.4000	3.13
(c) BeO Single Crystal	1 KC	—	18.9900	—	—

at room temperature. It should be noted that the D values for dissipation factor have not yet been computed since this is dependent upon final calibration of the instrument and will be reported at a later date. The purpose of this series of tests was to verify the capacitance range of the sample holder and evaluate test procedures. One measurement made on a single crystal specimen showed a C, or total capacitance of 13.990 picofarads indicating that the specimen size and geometry is compatable with the design of the test instrument.

(2) Optical Properties

In the first bi-monthly report preliminary infra-red transmission data was presented on BeO single crystals measured on a Beckman IR-8 spectrophotometer. Additional measurements have now been made on crystals prepared in a mosiac structure in which aperture sizes were increased to accomodate up to 6 monocrystals. As previously, the transmission spectrum was from 2.5 to 16 microns. For comparison purposes corresponding data was obtained on 95% dense cold-pressed and sintered beryllium oxide and theoretical density hot-pressed beryllium oxide of 99% purity. The three curves are shown in Figure (4). It may be observed that a noticeable absorption peak occurs in the BeO single crystal at about 7.3 microns and a minor peak occurs at 6.5 microns. These absorption peaks were reproducible over several BeO monocrystalline samples mounted in various ways with both slow and fast scan on the spectrophotometer indicating a fundamental behavior of the crystal structure.

(3) Thermal Conductivity Measurements

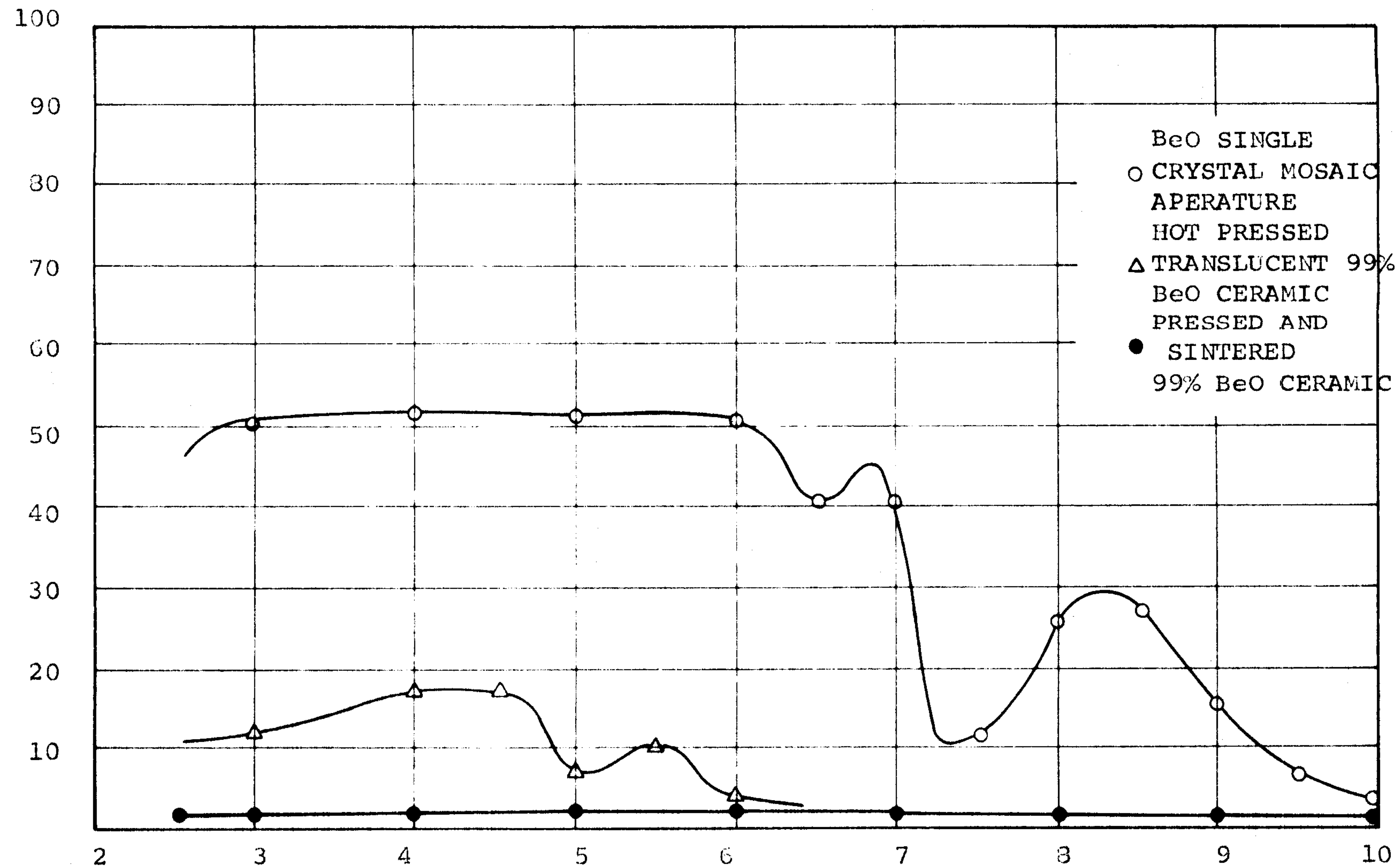
A review of the techniques for measurement of thermal conductivity has led to the selection of two approaches for making measurements on small BeO single crystals. These techniques are as follows:

(a) Comparative Method

This measurement technique is similar to the so-called cut-bar technique described in ASTM Test Procedure C-408-58 which has been utilized for the measurement of thermal conductivity of ceramic materials. In general, the cut-bar method consists of a series arrangement of a material of known conductivity such as copper with the unknown interposed between two sections of the known material. Thermocouples placed at predetermined spacings in both the known and the unknown allow calculation of Q heat flow once a thermal gradient is established, and K may be calculated based on the ΔT across the sample. In general, this technique is carried out in vacuum and is a relatively simple method. The only complications that arise are usually in the attachment of the sample to the known material. In the measurement of singlecrystal beryllium oxide the size and geometry

FIGURE 4

INFRA-RED TRAMSMISSION OF BeO CRYSTAL MOSAIC APERTURE



of the known specimen material is extremely small and therefore for these tests it has been decided to utilize the fiber or whisker type of single crystal which will provide data in one crystallographic direction. The apparatus consists basically of an electrical heat source, a differential thermocouple probe which acts as the known standard on the hot side and to which the tip of the crystal is attached. The heat sink is a liquid low melting alloy material into which the cold tip of the crystal may be immersed so as to establish the thermal gradient. The entire apparatus is designed to be operated in vacuum and should provide data at temperatures up to approximately 200°C above which radiation losses could become an error source. At the time of this report the design of the apparatus was complete and major portions of it have been fabricated and are being assembled. It is anticipated within the next month initial data will be forthcoming.

(b) The Dynamic Method

Arrangements have been made with Queens Laboratory of Edison, New Jersey to develop a dynamic or pulse technique for the measurement of the thermal conductivity of the platelet form of BeO single crystal.

Through the efforts of Dr. H. T. Smyth and Dr. W. Bauer, the physical calculations have been made, and preliminary experiments started to evaluate this method as a means of measuring thermal conductivity. A small sub-contract has been initiated to cover the initial stages of this work and should be sufficient to establish the feasibility of the method. If it is successful, this study technique can be expanded further. It basically consists of the introduction of a chopped light source, onto one side of the crystal, each side of the platelet having a vapor deposited bi-metallic film thermocouple. Based on the frequency of the heat energy and the temperature gradient established across the crystal the thermal conductivity may be calculated. Initial tests conducted with glass microscope slides and soon with polycrystalline BeO simulated crystals should establish the applicability of such a technique to the measurement of monocrystalline BeO properties.

(3) PLANS FOR NEXT REPORTING PERIOD

It is anticipated that during the next reporting period a considerable quantity of BeO crystal platelets will be accumulated which will be sufficient for most of the data generation necessary under the present phase of the program. Most of these crystals will be prepared by the water-vapor transport technique and the best will be selected for measurement purposes. Supporting X-ray and spectrographic data will also be obtained on any crystals evaluated. The solution method work will be continued to the point where crystals obtained will be measured on a comparative basis with those prepared by the water-vapor method. Dielectric constant and loss measurements using the re-designed sample holder will be conducted at room temperature and possibily initial measurements to 500°C will be available. Adaption of the sample holder apparatus to volume resistivity measurements will also be completed and initial property data obtained. Techniques for thermal conductivity measurement will be explored and it is anticipated that some initial data will be available on the anisotropic properties of BeO crystals in the a and c crystallographic direction. As with the other measurement techniques, calibration data will be obtained using polycrystalline simulated crystal samples for comparison purposes.

(4) PROJECT PERSONNEL

During the reporting period the following National Beryllia Corporation personnel participated in the program, Dr. E. Ryshkewitch, P. S. Hessinger, K. Styhr, R. L. Sharkitt, and G. Ferment.

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